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<p>(54) Title: KRAFT WOOD FIBERS FOR CARBOXYALKYL CELLULOSE (57) Abstract <p>Disclosed is a method for producing kraft wood fiber having an alpha-cellulose content greater than 97 % and a viscosity greater than 40 centipoise. The method involves prehydrolyzing hardwood chips with water, kraft cooking, bleaching and caustic treatment. The resulting pulp can be converted to carboxymethyl cellulose superabsorbents having improved properties, particularly a high "absorbency under load".</p></p>		

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KRAFT WOOD FIBERS FOR CARBOXYALKYL CELLULOSE

Background of the Invention

The use of absorbent materials, commonly known as superabsorbents, in disposable absorbent personal care products is known. Such absorbent materials are generally employed in absorbent products such as diapers, training pants, adult incontinence products, feminine care products, and the like, in order to
5 increase the absorbent capacity of such products while reducing their overall bulk. Such absorbent materials are generally present in absorbent products in a fibrous matrix, such as a matrix of wood pulp fluff. A matrix of wood pulp fluff generally has an absorbent capacity of about 6 grams of liquid per gram of fluff. The absorbent materials described above generally have an absorbent capacity of at
10 least about 10, preferably of about 20, and often of up to 100 times their weight in water. Clearly, incorporation of such absorbent materials in personal care products can reduce the overall bulk while increasing the absorbent capacity of such products.

A wide variety of materials have been described for use as absorbent
15 materials in such personal care products. Such materials include natural-based materials such as agar, pectin, gums, carboxyalkyl starch, carboxyalkyl cellulose including carboxymethyl cellulose, and the like, as well as synthetic materials such as polyacrylates, polyacrylamides, hydrolyzed polyacrylonitrile, and the like. While the natural-based, absorbent materials are known for use in personal care
20 products, they have not gained wide usage in such products. Such lack of use results, at least in part, from absorbent properties that are inferior compared to the synthetic absorbent materials such as the polyacrylates. Specifically, many of the natural-based materials tend to form soft, gelatinous masses when swollen with a liquid. When employed in absorbent products, the presence of such soft
25 gelatinous masses tends to prevent the transport of liquid within the fibrous matrix in which the absorbent materials are incorporated. This phenomenon is known as gel-blocking. Once gel-blocking occurs, subsequent insults of liquid cannot be efficiently absorbed by the product, and the product tends to leak. Further, many of the natural-based materials exhibit poor absorption properties, particularly when
30 subjected to external pressures. In contrast, the synthetic, absorbent materials

are often capable of absorbing large quantities of liquid while maintaining a generally stiff, non-gelatinous character. Accordingly, the synthetic, absorbent material can be incorporated in absorbent products while minimizing the likelihood of gel-blocking.

- 5 Carboxyalkyl polysaccharide and carboxyalkyl cellulose materials are well known in the art. Unfortunately, many known polysaccharide and cellulose materials do not possess absorptive properties comparable to many of the synthetic, highly absorptive materials.

10

Summary of the Invention

The invention is directed to a method for producing kraft wood pulp having an alpha-cellulose content greater than 97% and a viscosity greater than 40 centipoise (measured on a aqueous pulp via 0.5% CED method). The method involves prehydrolyzing hardwood chips with water, kraft cooking the wood chips, bleaching and then caustic treating of the fibers. The resulting pulp can be converted to a carboxyalkyl polysaccharide, preferably carboxyalkyl cellulose, and most preferably carboxymethyl cellulose superabsorbents having improved properties, particularly a high Absorbency Under Load of about 20 or greater, more specifically from 20 to about 25.

Brief Description of the Drawing

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Figure 1 illustrates the apparatus for determining the Absorbency Under Load values of an absorbent material.

Detailed Description of the Invention

- 20 In one aspect, the present invention concerns a method for producing kraft wood pulp having an alpha-cellulose content greater than 97% and a viscosity of 30 centipoise or greater, more specifically 40 centipoise or greater (measured on an aqueous pulp via 0.5% CED method in accordance with Technical Association of Pulp and Paper Industry (TAPPI) test method T230 om-89). In another aspect,

the wood pulp has a viscosity greater than about 42 centipoise. Preferably, the wood pulp comprises hardwood.

Although the basis for the wood pulp of the present invention is hardwood such as oaks, eucalyptuses, poplars, beeches, and aspens, a wide variety of
5 cellulosic fibers can be included in the process of the present invention. Illustrative cellulosic fibers include, but are not limited to, wood and wood products, such as wood pulp fibers; non-woody paper-making fibers from cotton, from straws and grasses, such as rice and esparto, from canes and reeds, such as bagasse, from bamboos, from stalks with bast fibers, such as jute, flax, kenaf, cannabis, linen
10 and ramie, and from leaf fibers, such as abaca and sisal. It is also possible to use mixtures of one or more cellulosic fibers. Preferably, the cellulosic fiber used is from a wood source. Suitable wood sources include softwood sources such as pines, spruces, and firs, and hardwood sources such as oaks, eucalyptuses, poplars, beeches, and aspens.

15 As used herein, the term "fiber" or "fibrous" is meant to refer to a particulate material having a major dimension less than 10mm, preferably less than 5mm, often between about 0.1mm and 3mm, wherein the length to diameter ratio (aspect ratio) of such particulate material is greater than about 10. Conversely, a "nonfiber" or "nonfibrous" material is meant to refer to a particulate material
20 wherein the length to diameter ratio of such particulate material is about 10 or less.

It is generally desired that the cellulosic fibers used herein be wettable. As used herein, the term "wetable" is meant to refer to a fiber or material which exhibits a water in air contact angle of less than 90°. Suitably, the cellulosic fibers useful in the present invention exhibit a water in air contact angle between about
25 10° to about 50° and more suitably between about 20° to about 30°. Suitably, a wettable fiber refers to a fiber which exhibits a water in air contact angle of less than 90°, at a temperature between about 0°C and less than about 100°C, and typically at ambient conditions, such as about 23° to 28°C.

Suitable cellulosic fibers are those which are naturally wettable. However,
30 naturally nonwettable fibers can also be used. It is possible to treat the fiber surfaces by an appropriate method to render them more or less wettable. When surface treated fibers are employed, the surface treatment is desirably nonfugitive; that is, the surface treatment desirably does not wash off the surface of the fiber

with the first liquid insult or contact. For the purposes of this application, a surface treatment on a generally nonwetable fiber will be considered to be nonfugitive when a majority of the fibers demonstrate a water in air contact angle of less than 90° for three consecutive contact angle measurements, with drying between each measurement. That is, the same fiber is subjected to three separate contact angle determinations and, if all three of the contact angle determinations indicate a contact angle of water in air of less than 90°, the surface treatment on the fiber will be considered to be nonfugitive. If the surface treatment is fugitive, the surface treatment will tend to wash off of the fiber during the first contact angle measurement, thus exposing the nonwetable surface of the underlying fiber, and will demonstrate subsequent contact angle measurements greater than 90°. Beneficial wettability agents include polyalkylene glycols, such as polyethylene glycols. The wettability agent is used in an amount comprising beneficially less than about 5 weight percent, suitably less than about 3 weight percent, and more suitably less than about 2 weight percent, of the total weight of the fiber, material, or absorbent structure being treated.

In the present invention, it is desired that the cellulosic fibers be used in a form wherein the cellulosic fibers have already been refined into a pulp. As such, the cellulosic fibers will be substantially in the form of individual cellulosic fibers although such individual cellulosic fibers may be in an aggregate form such as a pulp sheet. The current process, then, is in contrast to known steam explosion processes that generally treat cellulosic fibers that are typically in the form of virgin wood chips or the like. Thus, the current process is a post-pulping, cellulosic fiber modifying process as compared to known steam explosion processes that are generally used for high-yield pulp manufacturing or waste-recycle processes.

The starting material for the method of the present invention will normally be wood chips in which the fibers are of a length suitable for paper making. Shavings could also be used but sawdust would be undesirable except as a minor part of the total furnish as the fibers are partially cut. The chips should also, as is well known, be suitable in the sense of being free from bark and foreign matter.

It is desirable for the purposes of this invention that coarse chips be avoided. One problem with coarse chips is that cooking would not be complete. It is best to use shredded or thin chips.

The method of the present invention involves treatment of the hardwood fibers or chips in four basic steps: prehydrolysis, kraft cooking, bleaching, and a caustic treatment. This treatment produces a kraft wood pulp having an alpha-cellulose content greater than 97% and a viscosity of 30 centipoise or greater (when measured via 0.5% CED method). Alpha-cellulose is the major component of wood and paper pulp. It is that portion of cellulose that is insoluble in strong sodium hydroxide solution. Methods of determining the alpha content of pulps are detailed in TAPPI Method T203 and ASTM D-588-42. Conventional treatments of hardwoods have been known to provide high alpha-cellulose kraft pulps, but the viscosity of these pulps is fairly low, generally below about 20 centipoise.

Prehydrolysis.

The first stage in the method of the present invention wherein procedures can be utilized which improve the amount of hemicellulose removed from the lignocellulosic material while minimizing the amount of degradation of the cellulose, is the hydrolysis step. Wood chips in water at liquor/wood ratio of 4/1 in a M/K digester were heated to 170 degrees C with time to temperature of 60 minutes and time at temperature of 20 minutes. The hydrolysis liquor was drained from the digester after the hydrolysis process is done.

The particular hydrolysis used in the method of this invention is dependent on the type of wood and the degree of removing of hemicellulose. The hydrolysis has a great effect on the viscosity of the final high alpha-cellulose. In order to achieve desirable degree of hydrolysis, the H factor was used as a control tool. The definition of H factor can be found in a typical pulping book such as Pulping Processes written by Rydholm, published by Interscience Publishers, 1965. Basically, the H Factor is a variable used in the Kraft cooking process to combine the variables of temperature and time into a single variable representing the extent of the cooking. For the hydrolysis process, the H Factor is used to characterize the degree of hydrolysis. For the present invention, the hydrolysis temperature and time should be adjusted to obtain an H-factor ranging from about 300 to about 1000, more specifically from about 500 to about 800, and still more specifically from about 600 to about 700, with a corresponding minimum chip yield of about 80%. The preferable chip yield is 90% in this invention. The yield is defined as the

ratio of the resulted chip weight (oven dried basis) to the original chip weight (oven dried basis).

Kraft Cooking.

5 In the cooking step, the hydrolyzed chips were cooked in a M/K digester in a cooking liquor of sodium hydroxide and sodium sulfide at a liquor/wood ratio of 4/1 heated to 170 degrees C. for 35 to 60 minutes. The cooking liquor contained 15% effective alkaline and 25% sulfidity. The definition and calculation of effective alkaline and sulfidity can be found in a typical pulping book such as Pulping Processes written by Rydholm, published by Interscience Publishers, 1965. For 10 the present invention, the effective alkaline can ranged from 10 to 20% and sulfidity from 15 to 40%. The H Factor is used to characterize the degree of cooking. The H Factor used to obtain desirable pulp is dependent on the effective alkaline and sulfidity. For the present invention, the effective alkaline, sulfidity and 15 H Factor should be adjusted to obtain an unbleached pulp with a minimum Kappa number of 5, in order to achieve desirable final product. The Kappa number is used to represent the degree of lignin removal. The Kappa number was measured according to TAPPI test method T236 cm-85.

20

Bleaching.

 In the next step, the unbleached fiber was subjected to a bleaching process to remove residual lignin in a series of steps, using selected combinations of chemical reactants. In the prior art, various combinations of chemical treatments 25 have been suggested. Furthermore, individual treatment steps have been rearranged in an almost limitless number of combinations and permutations. Therefore, in order to simplify the explanation of the various bleaching processes, the use of letter codes is conventionally employed in the combination to describe the particular chemical reactants employed and the sequence of the steps of the 30 process. The letter codes which will be used hereafter, where appropriate, are as follows:

C= chlorination	Reaction with elemental chlorine in acidic medium
E= Alkaline Extraction	Dissolution of reaction product with NaOH

E(O)= Oxidative Alkaline	Dissolution of reaction product with NaOH and Oxygen
D= Chlorine Dioxide	Reaction with elemental chlorine Dioxide in acidic medium
P= Peroxide	Reaction with peroxide in alkaline medium
5 O=Oxygen	Reaction with elemental oxygen in alkaline medium
Z= Ozone	Reaction with ozone
C/D	A mixture of chlorine and chlorine dioxide
H= Hypochlorite	Reaction with hypochlorite in an alkaline solution

10 For the present invention, many combinations such as D-E-D, C/D- E- D can be used to remove residual lignin and raise pulp brightness to at least about 70%, and preferable to 85% brightness except that the C(chlorination) and H(hypochlorite) will not be used because they will degrade fiber and provide low viscosity.

15

Caustic Extraction.

The next step is a caustic extraction to further remove residual hemicellulose in the bleached fiber. The conditions of caustic extraction is to treat the bleached fiber in a 6 to 12% caustic sodium hydroxide solution for 10 to 100
20 minutes at 15 to 65 degree C. A specific conditions is to treat bleached fiber in the 7.5% caustic solution for 60 minutes at 25 degrees C. to obtain an alpha-cellulose content higher than 97%.

The treated wood pulp, prepared as described herein, can then be converted to carboxyalkyl polysaccharide, preferably carboxyalkyl cellulose, and
25 most preferably carboxymethyl cellulose (CMC) superabsorbents by methods that are well known in the art. A preferred conversion process is described in U.S. Patent No. 5,247,072 (Ning et al.) assigned to the assignee of the present invention, and incorporated herein in its entirety. Preferably, the resulting carboxyalkyl polysaccharide, carboxyalkyl cellulose, or carboxymethyl cellulose
30 has a relatively high molecular weight. It is generally most convenient to express the molecular weight of a carboxyalkyl cellulose in terms of its viscosity in a 2.0 weight percent aqueous solution. Preferably the carboxymethyl cellulose has a viscosity in a 2.0 weight percent aqueous solution of from about 50 centipoise to

about 80,000 centipoise, preferably from about 2,000 centipoise to about 80,000 centipoise, and most preferably from about 20,000 centipoise to about 80,000 centipoise.

The carboxyalkyl cellulose will suitable have a pH within the range of from
5 about 5.0 to about 11.0, beneficially from about 6.0 to about 10.0, and preferably from about 6.5 to about 9. It is generally desired that the carboxyalkyl cellulose has a generally neutral character.

It is desired that the carboxyalkyl cellulose have an Absorbency Under Load (AUL) of at least about 17, beneficially at least about 20, most beneficially at least
10 about 24, and preferably at least about 27 grams per gram.

Examples

The following examples present a nonlimiting illustration of the invention. All parts, percentages, ratios, etc. are given in weight unless otherwise noted.

15

Example 1

For Example 1, Terrace Bay Aspen wood chips were mixed with water in a 4:1 water:wood ratio. This mixture was cooked for 60 minutes up to a temperature of about 170°C and then held at 170°C for 20 minutes. At the end of this
20 prehydrolysis step, the liquid was drained. The prehydrolyzed aspen chips were mixed with an alkali solution (14.5% effective alkali, 25% sulfidity) in a 4:1 solution:wood chip ratio. This mixture was cooked for 60 minutes up to a temperature of about 170°C and then held at 170°C for 35 minutes. At the end of this kraft cooking step, the liquid was drained. For the bleaching step, the kraft
25 cooked prehydrolyzed aspen fibers were subjected to three stages. The wood fibers were diluted to 10% in an aqueous solution having 0.94% chlorine dioxide and were held at 135°F (57°C) for 60 minutes. A hot caustic extraction stage followed, where the fibers were diluted to 10% in an aqueous solution having 1.5% sodium hydroxide and were held at 160°F for 70 minutes. The chlorine dioxide
30 stage was repeated except that the wood fibers were diluted to 10% in an aqueous solution having 0.6% chlorine dioxide and were held at 160°F (71°C) for 150 minutes. This was followed by a caustic treatment (cold caustic extraction), where the fibers were diluted to 10% in an aqueous solution having a sodium

hydroxide concentration of 7.5 percent and were held at 77°F (25°C) for 60 minutes.

The resulting kraft pulp had an alpha-cellulose content of 97.8% and a viscosity of 42.9 centipoise.

5

Example 2

Example 2 was prepared as described for Example 1, except that mixed Southern Hardwood chips were used instead of Aspen.

The resulting kraft pulp had an alpha-cellulose content of 98.7% and a
10 viscosity of 40.5 centipoise.

Comparative Example A

Comparative Example A was a kraft wood pulp (available from ITT Rayonier, under the trade name "Ultranier"). It is believed this was a pine wood
15 pulp.

Comparative Example B

Comparative Example B was a southern softwood kraft pulp (available from U. S. Alliance Corporation under the designation "CR54 southern softwood kraft
20 pulp").

The overall properties Examples 1 and 2 and Comparative Examples A and B are listed in Table 1, below. Table 1 includes the percentage of alpha-cellulose, degree of polymerization in water (DPw), and viscosity in centipoise (measured via 0.5% CED method, TAPPI).
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25

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Table 1
Wood Pulp Properties

<u>Example</u>	<u>Wood Species</u>	<u>% alpha-cellulose</u>	<u>DPw</u>	<u>Viscosity</u>
1	Aspen	97.8	3593	42.9
2	Mixed Southern Hardwood	98.7	3431	40.5
Comp. A	assumed, Pine	98	1680	7
Comp. B	Southern Pine	87.6	2396	22

5 The Absorbency Under Load (AUL) is a test which measures the ability of an absorbent material to absorb a liquid (0.9 weight percent solution of sodium chloride in distilled water) while under an applied load or restraining force.

Referring to FIG. 1, the apparatus and method for determining AUL will be described. Shown is a perspective view of the apparatus in position during a test.
10 Shown is a laboratory jack 1 having an adjustable knob 2 for raising and lowering the platform 3. A laboratory stand 4 supports a spring 5 connected to a modified thickness meter probe 6, which passes through the housing 7 of the meter, which is rigidly supported by the laboratory stand. A plastic sample cup 8, which contains the superabsorbent material sample to be tested, has a liquid-permeable
15 bottom and rests within a Petri dish 9, which contains the saline solution to be absorbed. A weight 10 rests on top of a spacer disc (not visible) resting on top of the superabsorbent material sample (not visible).

The sample cup consists of a plastic cylinder having a 1 inch inside diameter and an outside diameter of 1.25 inch. The bottom of the sample cup is
20 formed by adhering a 100 mesh metal screen having 150 micron opening to the end of the cylinder by heating the screen above the melting point of the plastic and pressing the plastic cylinder against the hot screen to melt the plastic and bond the screen to the plastic cylinder.

The modified thickness meter used to measure the expansion of the sample
25 while absorbing the saline solution is a Mitutoyo Digimatic Indicator, IDC Series 543, Model 543-180, having a range of 0-0.5 inch and an accuracy of 0.00005 inch (Mitutoyo Corporation, 31-19, Shiba 5-chome, Minato-ku, Tokyo 108, Japan).

As supplied from Mitutoyo Corporation, the thickness meter contains a spring attached to the probe within the meter housing. This spring is removed to provide a free falling probe, which has a downward force of about 27 grams. In addition, the cap over the top of the probe located on the top of the meter housing is also removed to enable attachment of the probe to the suspension spring 5 (available from McMaster-Carr Supply Co., Chicago, Ill., Item No. 964OK41), which serves to counter or reduce the downward force of the probe to about 1 gram, ± 0.5 gram. A wire hook can be glued to the top of the probe for attachment to the suspension spring. The bottom tip of the probe is also provided with an extension needle 10 (Mitutoyo Corporation, Part No. 131279) to enable the probe to be inserted into the sample cup.

To carry out the test, a 0.160 gram sample of the absorbent material, which has been sieved to a particle size between 300 and 600 microns, is placed into the sample cup. The sample is then covered with a plastic spacer disc, weighing 4.4 15 grams, which is slightly smaller than the inside diameter of the sample cup and serves to protect the sample from being disturbed during the test. The 100 grams weight is then placed on top of the spacer disc, thereby applying a load of 0.3 pounds per square inch. The sample cup is placed in the Petri dish on the platform of the laboratory jack raised up until it contacts the tip of the probe. The meter is zeroed. A sufficient amount of saline solution is added to the Petri dish 20 (50-100 milliliters) to begin the test. The distance the weight is raised by the expanding sample as it absorbs the saline solution is measured by the probe. This distance, multiplied by the cross-sectional area inside the sample cup, is a measure of the expansion volume of the sample due to absorption. Factoring in the density of the saline solution and the weight of the sample, the amount of 25 saline solution absorbed is readily calculated. The weight of saline solution absorbed after 60 minutes is the AUL value, expressed as grams saline solution absorbed per gram of absorbent. If desired, the readings of the modified thickness meter can be continuously input to a computer (Mitutoyo Digimatic 30 Miniprocessor DP-2 DX) to make the calculations and provide AUL readings. As a cross-check, the AUL can also be determined by determining the weight difference between the sample cup before and after the test, the weight difference being the amount of solution absorbed by the sample.

Examples 1 and 2 and Comparative Examples A and B were converted into carboxymethyl cellulose (CMC) superabsorbants as taught by U.S. Patent No. 5,247,072. More specifically, 15 grams of cellulose (0.0943 mole) was first immersed in 400 ml isopropanol in a reaction kettle equipped with a mechanical stirrer, an inert gas inlet and a temperature control probe. 8.31 g (0.208 mole) NaOH dissolved in 35 ml water solution (if the starting cellulose was in wet pulp form with about 30% consistency, no water is needed, adding in NaOH pellets directly) was added. The pulp slurry was stirred for half an hour at room temperature (1 hour if dry NaOH is used). 8.9 g (0.0945 mole) of Chloroacetic acid (CAA) was then added and the temperature raised to 60 C under stirring. The reaction continued for three hours at 60C. After that the slurry was filtered, the product washed twice with 70:30 (by volume) mixture solvent of methanol and water (400 ml solution for each wash). The pH of the slurry in washing liquid was adjusted to around 7.4 with acetic acid during the first wash cycle. Finally the CMC fibers was washed one more time with 100% methanol and allowed to dry at 50C. This will generally yield about 21 grams of dry CMC with a typical degree of substitution (D.S.) at 0.9.

Procedures for preparing CMC-SAP:

The CMC fibers were then dissolved in water to make a 2% solution, dried at 50C and ground into granules. Particle sizes ranging 300 – 600 microns were collected for thermo-curing and absorbency test. This part of the procedure is in accordance with U.S. 5,247,072, previously incorporated by reference. The resulting superabsorbants were tested for Absorbency Under Load, as described by the above test procedure. The AUL results, as a function of curing time, are given in Table 2, below.

Table 2
AUL results, reported in grams/gram

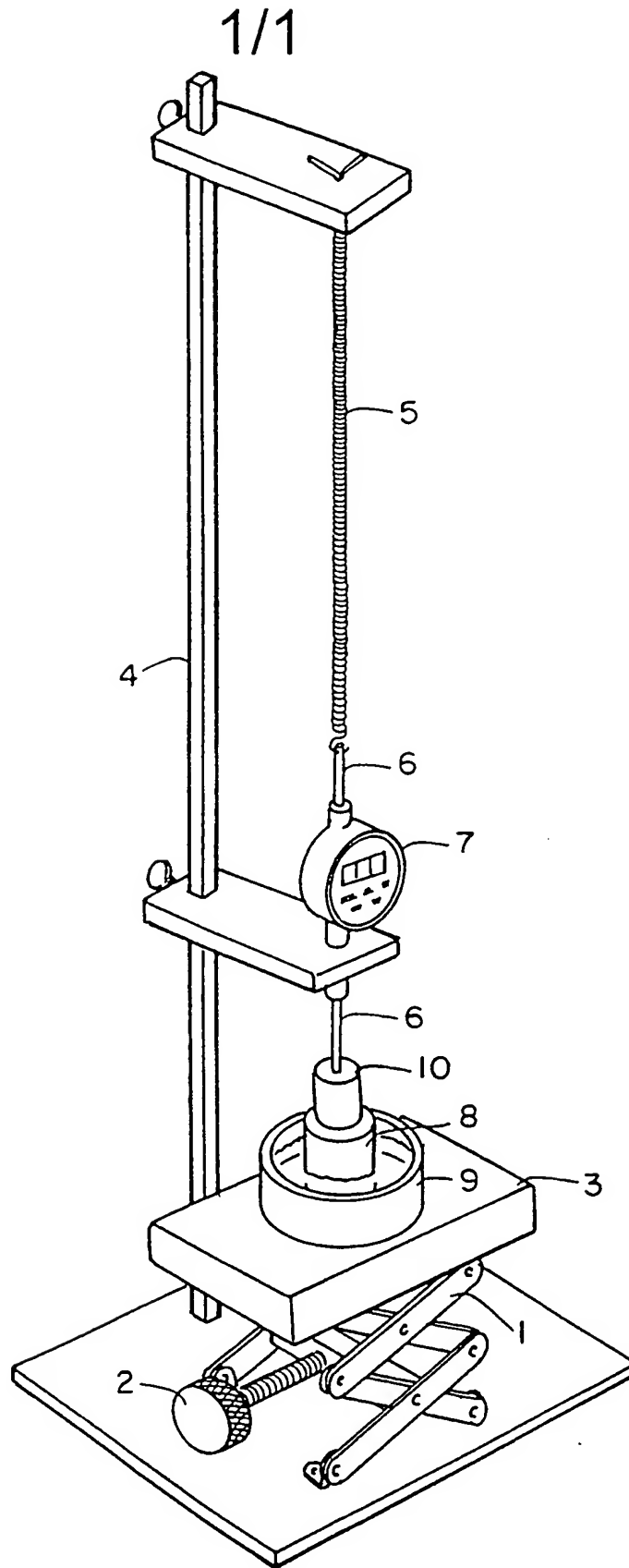
<u>Example</u>	<u>Time (minutes)</u>						
	0	15	30	45	60	90	120
1	21.4	--	--	--	23	22.2	21.8
2	22.7	22.2	21.2	21.8	21.5	21.6	20.8
Comp. A	16.5	--	19.4	19.5	19.6	19.4	19.8
Comp. B	12	13.2	13.4	13.7	13.3	13.4	13.5

-- not tested

It will be appreciated that the foregoing description and examples, given for purposes of illustration, are not to be construed as limiting the scope of this invention, which is defined by the following claims and all equivalents thereto.

We claim:

1. A method for producing an absorbent carboxyalkyl polysaccharide composition from a fiber pulp having an alpha-cellulose content greater than 97% and a viscosity greater than 30 centipoise, the method comprising (a) prehydrolyzing
5 hardwood chips with water; (b) kraft cooking the prehydrolyzed wood chips to reduce the wood chips to fibers; (c) bleaching the cooled fibers; (d) treating the bleached fibers with caustic to form a treated fiber pulp; and (e) converting the treated fiber pulp to a carboxyalkyl polysaccharide having improved absorbency.
2. The method of claim 1 wherein the hardwood chips are prehydrolyzed at an H factor of from about 300 to about 1000 with a corresponding maximum chip yield of about 80 percent.
3. The method of claim 1 wherein the hardwood chips are prehydrolyzed at an H factor of from about 500 to about 800.
4. The method of claim 1 wherein the hardwood chips are prehydrolyzed at an H factor of about 600 to about 700.
5. The method of claim 1 wherein the prehydrolyzed hardwood chips were cooked in a cooking liquid of sodium hydroxide and sodium sulfide to obtain an unbleached pulp with a Kappa number of 5 or greater.
6. The method of claim 1 wherein the caustic treatment of the bleached wood fibers is carried out with a sodium hydroxide solution at from about 15 to about 65 degrees C. from about 10- to about 100 minutes.
7. The method of claim 1 wherein the carboxyalkyl polysaccharide is carboxymethyl cellulose having an AUL of about 20 or greater.
8. The method of claim 7 wherein the AUL is from 20 to about 25.



INTERNATIONAL SEARCH REPORT

Inter. .onal Application No
PCT/US 99/31287

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 D21C9/00 C08B11/12

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 D21C C08B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5 550 189 A (QIN JIAN ET AL) 27 August 1996 (1996-08-27) examples 6,10	1
A	tables 9,10,24	7,8
Y	J.P. CASEY: "Pulp and Paper; Chemistry and Chemical Technology, 3rd edition, vol. I" 1980 , JOHN WILEY & SONS , NEW YORK XP002138323 pages 25, 26, 411-421	1
A		2-5
Y	US 4 361 463 A (LINDBERG ERIK A S ET AL) 30 November 1982 (1982-11-30) column 1, line 9 - line 37; figure 1	1
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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

22 May 2000

Date of mailing of the international search report

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Name and mailing address of the ISA
European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl.
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INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 99/31287

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		Relevant to claim No.
Category *	Citation of document, with indication, where appropriate, of the relevant passages	
Y	<p>DATABASE PAPERCHEM 'Online! THE INSTITUTE OF PAPER SCIENCE AND TECHNOLOGY, ATLANTA, GA, US OWCZARZAK, J.: "Properties of Beechwood 'Fagus! Dissolving Pulp Manufactured with Acid-Steam Prehydrolysis" retrieved from DIALOG XP002138324 abstract & PRZEGL. PAPIER. 47, NO. 10: 353-355 (OCT. 1991). 'POL.!, ----</p>	1
Y	<p>DATABASE PAPERCHEM 'Online! THE INSTITUTE OF PAPER SCIENCE AND TECHNOLOGY, ATLANTA, GA, US NATEROVA, A. ET AL: "CONDITIONS FOR THE PREPARATION OF CARBOXYMETHYLCELLULOSE. (1). EFFECT OF THE AGENT DOSE AND REACTION TIME" retrieved from DIALOG XP002138325 abstract & VYSKUM. PR. ODBORU PAPIERA CELULOZY 18: V49-53 (1973). 'GER.;SLOVAK., ENGL., & RUSS. SUM.!, ----</p>	1
Y	<p>DATABASE PAPERCHEM 'Online! THE INSTITUTE OF PAPER SCIENCE AND TECHNOLOGY, ATLANTA, GA, US KARAIVANOVA, S. ET AL: "PREPARATION OF CARBOXYMETHYLCELLULOSE FOR THE TEXTILE INDUSTRY FROM BEECHWOOD PREHYDROLYSIS KRAFT PULP" retrieved from DIALOG XP002138326 abstract & KHIM. IND. (SOFIA) 37, NO. 2: 49-54 (1965). 'BULG.;RUSS. & GER. SUM.!, ----</p>	1
Y	<p>US 2 878 118 A (ROGERS LINWOOD N ET AL) 17 March 1959 (1959-03-17) the whole document</p>	1
A		5,6
A	<p>US 2 645 577 A (BATE STANLEY C ET AL) 14 July 1953 (1953-07-14) the whole document</p>	1
A	<p>US 2 882 965 A (WAYMAN MORRIS ET AL) 21 April 1959 (1959-04-21)</p>	
A	<p>US 5 247 072 A (NING XIN ET AL) 21 September 1993 (1993-09-21) cited in the application</p>	

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 99/31287

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5550189 A	27-08-1996	AU 687478 B	26-02-1998
		AU 1084595 A	22-05-1995
		BR 9407917 A	26-11-1996
		CA 2130427 A	30-04-1995
		CN 1139437 A	01-01-1997
		CZ 9601223 A	16-10-1996
		EP 0739357 A	30-10-1996
		HU 75504 A	28-05-1997
		JP 9504331 T	28-04-1997
		PL 317098 A	17-03-1997
		SK 49996 A	05-03-1997
		WO 9511925 A	04-05-1995
		AU 3694993 A	21-10-1993
		AU 690844 B	30-04-1998
		AU 5463896 A	01-08-1996
		CA 2076732 A	18-10-1993
		DE 69313908 D	23-10-1997
		DE 69313908 T	26-03-1998
		EP 0566118 A	20-10-1993
		ES 2107574 T	01-12-1997
		JP 6025303 A	01-02-1994
		MX 9301563 A	01-10-1993
US 4361463 A	30-11-1982	FI 802942 A	10-04-1981
US 2878118 A	17-03-1959	BE 526577 A	
		FR 1184508 A	22-07-1959
US 2645577 A	14-07-1953	GB 640490 A	
		GB 679832 A	
		US 2645576 A	14-07-1953
US 2882965 A	21-04-1959	GB 787307 A	
US 5247072 A	21-09-1993	AU 658455 B	13-04-1995
		AU 2729192 A	29-04-1993
		BR 9204036 A	04-05-1993
		CA 2073292 A	26-04-1993
		DE 69223587 D	29-01-1998
		DE 69223587 T	23-07-1998
		EP 0538904 A	28-04-1993
		ES 2111032 T	01-03-1998
		JP 5214001 A	24-08-1993
		MX 9205548 A	01-04-1993
		ZA 9207461 A	13-04-1993